

CHAPTER ONE

The Earth-atmosphere system

1.1 INTRODUCTION

The Earth's atmosphere is the gaseous envelope surrounding the planet. Like other planetary atmospheres, it figures centrally in transfers of energy between the sun, the Earth, and deep space. It also figures in transfers of energy from one region of the globe to another. By maintaining thermal equilibrium, such transfers determine the Earth's climate. However, among neighboring planets, the Earth's atmosphere is unique because it is related closely to ocean and surface processes that, together with the atmosphere, form the basis for life.

Because it is a fluid system, the atmosphere is capable of supporting a wide spectrum of motions. These range from turbulent eddies of a few meters to circulations with dimensions of the Earth itself. By rearranging mass, air motion influences other atmospheric components such as water vapor, ozone, and cloud, which figure prominently in radiative and chemical processes. Such influence makes the atmospheric circulation a key ingredient of the global energy budget.

1.1.1 Descriptions of atmospheric behavior

The mobility of a fluid system makes its description complex. Atmospheric motion redistributes mass and constituents into a variety of complex configurations. Like any fluid system, the atmosphere is governed by the laws of continuum mechanics. They can be derived from the laws of mechanics and thermodynamics that govern a discrete fluid body by generalizing those laws to a continuum of such systems. In the atmosphere, the discrete system to which these laws apply is an infinitesimal fluid element, or *air parcel*, which is defined by a fixed collection of matter.

Two frameworks are used to describe atmospheric behavior. The *Eulerian description* represents atmospheric behavior in terms of field properties, such as the instantaneous distributions of temperature, motion, and constituents. Governed by partial differential equations, the field description of atmospheric behavior is convenient for numerical applications. The *Lagrangian description* represents atmospheric behavior in terms of the properties of individual air parcels (e.g., in terms of their instantaneous positions, temperatures, and constituent concentrations). Because it focuses on transformations of properties within an air parcel and on interactions between that system and its environment, the Lagrangian description offers conceptual as well as certain diagnostic advantages. For this reason, the basic principles governing atmospheric behavior are developed in this text from a Lagrangian perspective.

In the Lagrangian framework, the system considered is an individual air parcel moving through the circulation. Although it may change in form through deformation and in composition through thermodynamic and chemical transformations, this system is uniquely identified by the matter comprising it initially. Mass can be transferred across the boundary of an air parcel through molecular diffusion and turbulent mixing. However, such transfers are slow enough to be ignored for many applications. An individual parcel can then change only through interaction with its environment and through internal transformations that alter its composition and state.

1.1.2 Mechanisms influencing atmospheric behavior

Of the factors influencing atmospheric behavior, gravity is the single most important. Even though it has no upper boundary, the atmosphere is contained by the gravitational field of the Earth, which prevents atmospheric mass from escaping to space. Because it is such a strong body force, gravity determines many atmospheric properties. Most immediate is the geometry of the atmosphere. Atmospheric mass is concentrated in the lowest 10 km - less than 1% of the Earth's radius. Gravitational attraction has compressed the atmosphere into a shallow layer above the Earth's surface in which mass and constituents are stratified vertically: They are layered.

Through stratification of mass, gravity imposes a strong kinematic constraint on atmospheric motion. Circulations with dimensions greater than a few tens of kilometers are quasi-horizontal. Vertical displacements of air are then much smaller than horizontal displacements. Under these circumstances, constituents such as water vapor and ozone fan out in layers or "strata." Vertical displacements are comparable to horizontal displacements only in small-scale circulations such as convective cells and fronts, which have horizontal dimensions comparable to the vertical scale of the mass distribution.

The compressibility of air complicates the description of atmospheric behavior by enabling the volume of a parcel to change as it experiences changes in surrounding pressure. Therefore, concentrations of mass and constituents for the parcel can change, even though the number of molecules remains fixed. The concentration of a chemical constituent can also change through internal transformations, which alter the number of a particular type of molecule. For example, condensation decreases the abundance of water vapor in an air parcel that passes through a cloud system. Photodissociation of O_2 will increase the abundance of ozone in a parcel that passes through a region of sunlight.

Exchanges of energy with its environment and transformations between one form of energy and another likewise alter the properties of an air parcel. By expanding, an

air parcel exchanges energy mechanically with its environment through work that it performs on the surroundings. Heat transfer, as occurs through absorption of radiant energy and conduction with the Earth's surface, represents a thermal exchange of energy with a parcel's environment. Absorption of water vapor by an air parcel (e.g., through contact with a warm ocean surface) has a similar effect. When the vapor condenses, latent heat of vaporization carried by the vapor is released to the surrounding molecules of dry air that comprise the parcel. If the condensed water then precipitates back to the Earth's surface, this process leads to a net transfer of heat from the Earth's surface to the parcel.

The Earth's rotation, like gravity, exerts an important influence on atmospheric motion and, hence, on distributions of atmospheric properties. Because the Earth is a noninertial reference frame, the conventional laws of mechanics do not hold; they must be modified to account for its acceleration. Apparent forces introduced by the Earth's rotation are responsible for properties of the large-scale circulation, in particular, the flow of air around centers of low and high pressure. Those forces also inhibit meridional, e.g., NS (North-South) motion. Consequently, they inhibit transfers of heat and constituents between the equator and poles. For this reason, rotation tends to stratify properties meridionally, just as gravity tends to stratify them vertically.

The physical processes described in the preceding paragraphs do not operate independently. They are interwoven in a complex fabric of radiation, chemistry, and dynamics that govern the Earth-atmosphere system. Interactions among these can be just as important as the individual processes themselves. For instance, radiative transfer controls the thermal structure of the atmosphere, which determines the circulation. Transport by the circulation, in turn, influences the distributions of radiatively active components such as water vapor, ozone, and cloud. In view of their interdependence, understanding how one of these processes influences behavior requires an understanding of how that process interacts with others. This feature makes the study of the Earth-atmosphere system an eclectic one, involving the integration of many different physical principles. This book develops the most fundamental of these.

1.2 COMPOSITION AND STRUCTURE

The Earth's atmosphere consists of a mixture of gases, mostly molecular nitrogen (78% by volume) and molecular oxygen (21% by volume); see Table 1.1. Water vapor, carbon dioxide, and ozone, along with other minor constituents, comprise the remaining 1% of the atmosphere. Although present in very small abundances, trace species such as water vapor and ozone play a key role in the energy balance of the Earth through their involvement in radiative processes. Because they are created and destroyed in particular regions and are linked to the circulation through transport, these and other minor species are highly variable. For this reason, trace species are treated separately from the primary atmospheric constituents, which are referred to simply as "dry air."

1.2.1 Description of air

The starting point for describing atmospheric behavior is the ideal gas law

$$\begin{aligned}
 pV &= nR^*T \\
 &= \frac{m}{M}R^*T \\
 &= mRT,
 \end{aligned}
 \tag{1.1}$$

Table 1.1. Atmospheric Composition. Constituents are listed with volume mixing ratios representative of the Troposphere or Stratosphere, how the latter are distributed vertically, and controlling processes

Constituent	Tropospheric Mixing Ratio	Vertical Distribution (Mixing Ratio)	Controlling Processes
N_2	.7808	Homogeneous	Vertical Mixing
O_2	.2095	Homogeneous	Vertical Mixing
* H_2O	≤ 0.030	Decreases sharply in Troposphere Increases in Stratosphere Highly Variable	Evaporation, Condensation, Transport Production by CH_4 Oxidation
Ar	.0093	Homogeneous	Vertical Mixing
* CO_2	380 ppmv	Homogeneous	Vertical Mixing Production by Surface and Anthropogenic Processes
* O_3	10 ppmv [§]	Increases sharply in Stratosphere Highly Variable	Photochemical Production in Stratosphere; secondarily through pollution in troposphere Destruction at Surface Transport
* CH_4	1.8 ppmv	Homogeneous in Troposphere Decreases in Middle Atmosphere	Production by Surface Processes Oxidation Produces H_2O
* N_2O	320 ppbv	Homogeneous in Troposphere Decreases in Middle Atmosphere	Production by Surface and Anthropogenic Processes Dissociation in Middle Atmosphere Produces NO Transport
* CO	70 ppbv	Decreases in Troposphere Increases in Stratosphere	Production Anthropogenically and by Oxidation of CH_4 Transport
NO	0.1 ppbv [§]	Increases Vertically	Production by Dissociation of N_2O Catalytic Destruction of O_3
* $CFC-11$	0.2 ppbv	Homogeneous in Troposphere	Industrial Production
* $CFC-12$	0.5 ppbv	Decreases in Stratosphere	Mixing in Troposphere
* $HFC-134A$	30 ppt		Photo-dissociation in Stratosphere

* Radiatively active

[§] Stratospheric value

which constitutes the equation of state for a pure (single-component) gas. In (1.1), p , T , and M denote the pressure, temperature, and molar weight of the gas, and V , m , and $n = \frac{m}{M}$ refer to the volume, mass, and molar abundance of a fixed collection of matter (e.g., an air parcel). The *specific gas constant* R is related to the *universal gas constant* R^* through

$$R = \frac{R^*}{M}. \quad (1.2)$$

Equivalent forms of the ideal gas law that do not depend on the dimension of the system are

$$\begin{aligned} p &= \rho RT \\ pv &= RT, \end{aligned} \quad (1.3)$$

where ρ and $v = \frac{1}{\rho}$ (also denoted α) are the density and *specific volume* of the gas.

Because it is a mixture of gases, air obeys similar relationships. So do its individual components. The *partial pressure* p_i of the i th component is that pressure the i th component would exert in isolation at the same volume and temperature as the mixture. It satisfies the equation of state

$$p_i V = m_i R_i T, \quad (1.4.1)$$

where R_i is the specific gas constant of the i th component. Similarly, the *partial volume* V_i is that volume the i th component would occupy in isolation at the same pressure and temperature as the mixture. It satisfies the equation of state

$$p V_i = m_i R_i T. \quad (1.4.2)$$

Dalton's law asserts that the pressure of a mixture of gases equals the sum of their partial pressures

$$p = \sum_i p_i. \quad (1.5)$$

Likewise, the volume of the mixture equals the sum of the partial volumes¹

$$V = \sum_i V_i. \quad (1.6)$$

The equation of state for the mixture can be obtained by summing (1.4) over all of the components

$$pV = T \sum_i m_i R_i.$$

Then, defining the mean specific gas constant

$$\bar{R} = \frac{\sum_i m_i R_i}{m} \quad (1.7)$$

yields the equation of state for the mixture

$$pV = m\bar{R}T. \quad (1.8)$$

The mean molar weight of the mixture is defined by

$$\bar{M} = \frac{m}{n}. \quad (1.9)$$

Because the molar abundance of the mixture is equal to the sum of the molar abundances of the individual components,

$$n = \sum_i \frac{m_i}{M_i},$$

(1.9) may be expressed

$$\bar{M} = \frac{R^* m}{\sum_i m_i \left(\frac{R^*}{M_i}\right)}.$$

¹ These are among several consequences of the Gibbs-Dalton law, which relates the properties of a mixture to properties of the individual components (e.g., Keenan, 1970).

Then applying (1.2) for the i th component together with (1.7) leads to

$$\bar{R} = \frac{R^*}{M}. \quad (1.10)$$

Equation (1.10) is analogous to (1.2) for a single-component gas.

Because of their involvement in radiative and chemical processes, variable components of air must be quantified. The “absolute concentration” of the i th species is measured by its density ρ_i or, alternatively, by its *number density*

$$[i] = \left(\frac{N_A}{M_i} \right) \rho_i \quad (1.11)$$

(also denoted n_i), where N_A is Avogadro’s number and M_i is the molar weight of the species. Partial pressure p_i and partial volume V_i are other measures of absolute concentration.

The compressibility of air makes absolute concentration an ambiguous measure of a constituent’s abundance. Even if a constituent is passive, namely if the number of molecules inside an individual parcel is fixed, its absolute concentration can change through changes of volume. For this reason, a constituent’s abundance is more faithfully described by the “relative concentration,” which is referenced to the overall abundance of air or simply dry air. The relative concentration of the i th species is measured by the *molar fraction*

$$N_i = \frac{n_i}{n}. \quad (1.12)$$

Dividing (1.4) by (1.8) and applying (1.2) for the i th component leads to

$$N_i = \frac{p_i}{p} = \frac{V_i}{V}. \quad (1.13)$$

Molar fraction uses as a reference the molar abundance of the mixture, which can vary through changes of individual species. A more convenient measure of relative concentration is mixing ratio. The *mass mixing ratio* of the i th species

$$r_i = \frac{m_i}{m_d}, \quad (1.14)$$

where the subscript d refers to dry air, is dimensionless. It is expressed in g kg^{-1} for tropospheric water vapor and in parts per million by mass (ppmm, or simply ppm) for stratospheric ozone. Unlike molar abundance, the reference mass m_d is constant for an individual air parcel. If the i th species is passive, namely if it does not undergo a transformation of phase or a chemical reaction, its mass m_i is also constant. The mixing ratio r_i is then fixed for an individual air parcel.

For a trace species, such as water vapor or ozone, the mixing ratio is closely related to the molar fraction

$$N_i \cong \frac{r_i}{\epsilon_i}, \quad (1.15.1)$$

where

$$\epsilon_i = \frac{M_i}{M_d}, \quad (1.15.2)$$

because the mass of air in the presence of such species is nearly identical to that of dry air. The *volume mixing ratio* provides similar information. It is distinguished from mass mixing ratio by dimensions such as parts per million by volume (ppmv) for stratospheric ozone (Probs. 1.2, 1.3). From (1.13) and (1.12), it follows that the volume mixing ratio is approximately equal to the molar fraction. Each measures the relative abundance of molecules of the i th species.

As noted, the mixing ratio of a passive species is fixed for an individual air parcel. A property that is invariant for individual parcels is said to be *conserved*. Although constant for individual air parcels, a conserved property is generally not constant in space and time. Unless that property happens to be homogeneous, its distribution must vary spatially and temporally, as parcels with different values exchange positions. A conserved property is a *material tracer* because particular values track the motion of individual air parcels. Thus, tracking particular values of r_i provides a description of how air is rearranged by the circulation and, therefore, of how all conserved species are redistributed.

1.2.2 Stratification of mass

By confining mass to a shallow layer above the Earth's surface, gravity exerts a profound influence on atmospheric behavior. If vertical accelerations are ignored, then Newton's second law of motion applied to the column of air between some level at pressure p and a level incrementally higher at pressure $p + dp$ (Fig. 1.1) reduces to a balance between the weight of that column and the net pressure force acting on it

$$pdA - (p + dp)dA = \rho g dV,$$

where g denotes the acceleration of gravity, or

$$\frac{dp}{dz} = -\rho g. \quad (1.16)$$

This simple form of mechanical equilibrium is known as *hydrostatic balance*. It is a good approximation even if the atmosphere is in motion because, for large-scale circulations, vertical displacements of air are small. This feature renders vertical acceleration two to three orders of magnitude smaller than the forces in (1.16). Applying the same analysis between the pressure p and the top of the atmosphere (where p vanishes) illustrates the origin of atmospheric pressure: The pressure at any level must equal the weight of the atmospheric column of unit cross-sectional area above that level.

Owing to the compressibility of air, the density in (1.16) is not constant. It depends on the air's pressure through the gas law. Eliminating ρ with (1.3) and integrating from the surface to an altitude z yields

$$\frac{p}{p_s} = e^{-\int_{z_s}^z \frac{dz'}{H(z')}}, \quad (1.17.1)$$

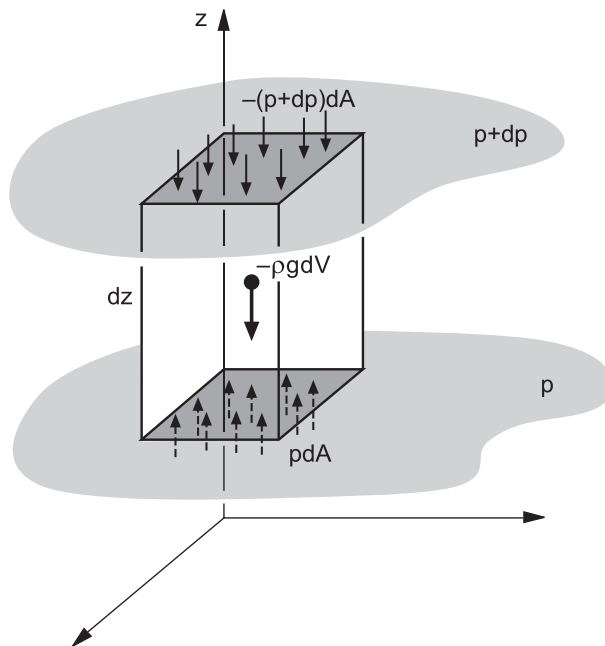


Figure 1.1 Hydrostatic balance for an incremental atmospheric column of cross-sectional area dA and height dz , bounded vertically by isobaric surfaces at pressures p and $p + dp$.

where

$$H(z) = \frac{RT(z)}{g} \quad (1.17.2)$$

is the pressure *scale height* and p_s is the surface pressure. The scale height represents the characteristic vertical dimension of the mass distribution. A function of altitude, it varies from about 8 km near the Earth's surface to 6 km in very cold regions of the atmosphere.

As illustrated by Fig. 1.2, global-mean pressure and density decrease with altitude approximately exponentially. Pressure decreases from about 1000 hPa or 10^5 Pascals (Pa) at the surface to only 10% of that value at an altitude of 15 km (two scale heights).² According to hydrostatic balance, 90% of the atmosphere's mass then lies beneath this level. Pressure decreases by another factor of 10 for each additional 15 km of altitude. Density decreases with altitude at about the same rate, from a surface value of about 1.2 kg m^{-3} . The sharp upward decrease of pressure implies that isobaric surfaces, along which $p = \text{const}$, are quasi-horizontal. Deflections of those surfaces introduce comparatively small horizontal variations of pressure that drive atmospheric motion.

² The historical unit of pressure, millibar (mb), has been replaced by its equivalent in the Standard International (SI) system of units, the hectoPascal (hPa), where $1 \text{ hPa} = 100 \text{ Pa} = 1 \text{ mb}$. See Appendix A for conversions between the SI system of units and others.

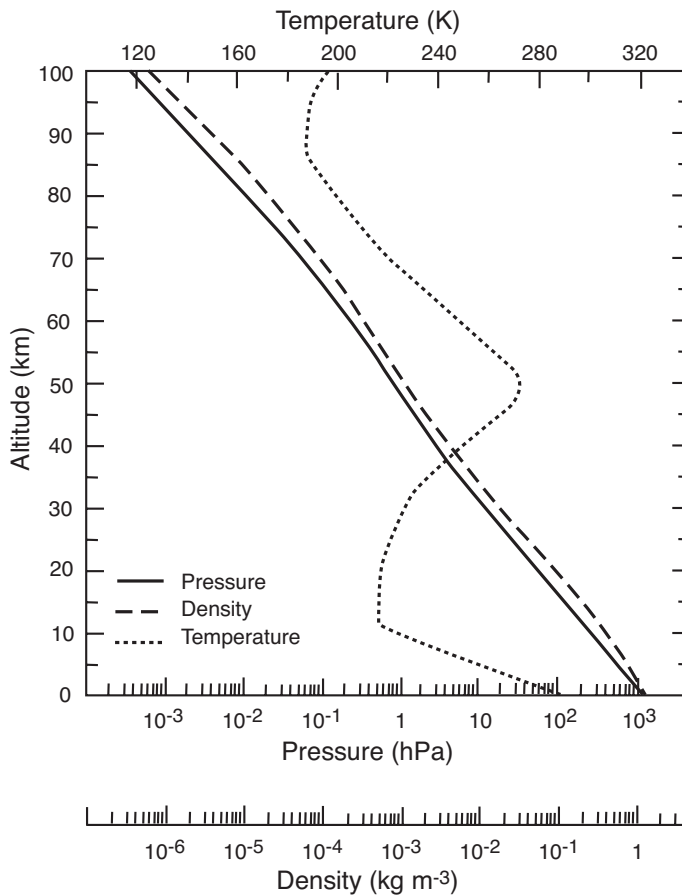


Figure 1.2 Global-mean pressure (solid), density (dashed), and temperature (dotted), as functions of altitude. *Source: U.S. Standard Atmosphere (1976).*

Above 100 km, pressure and density also decrease exponentially (Fig. 1.3), but at a rate which differs from that below and which varies gradually with altitude. The distinct change of behavior near 100 km marks a transition in the processes that control the stratification of mass and the composition of air. The mean free path of molecules is determined by the frequency of collisions. It varies inversely with air density. Consequently, the mean free path increases exponentially with altitude, from about 10^{-7} m at the surface to of order 1 m at 100 km. Because it controls molecular diffusion, the mean free path determines properties of air such as viscosity and thermal conductivity. Diffusion of momentum and heat supported by those properties dissipate atmospheric motion by destroying gradients of velocity and temperature.

Below 100 km, the mean free path is short enough for turbulent eddies in the circulation to be only weakly damped by molecular diffusion. At those altitudes, bulk transport by turbulent air motion dominates diffusive transport of atmospheric constituents. Turbulence stirs different gases with equal efficiency. Mixing ratios of

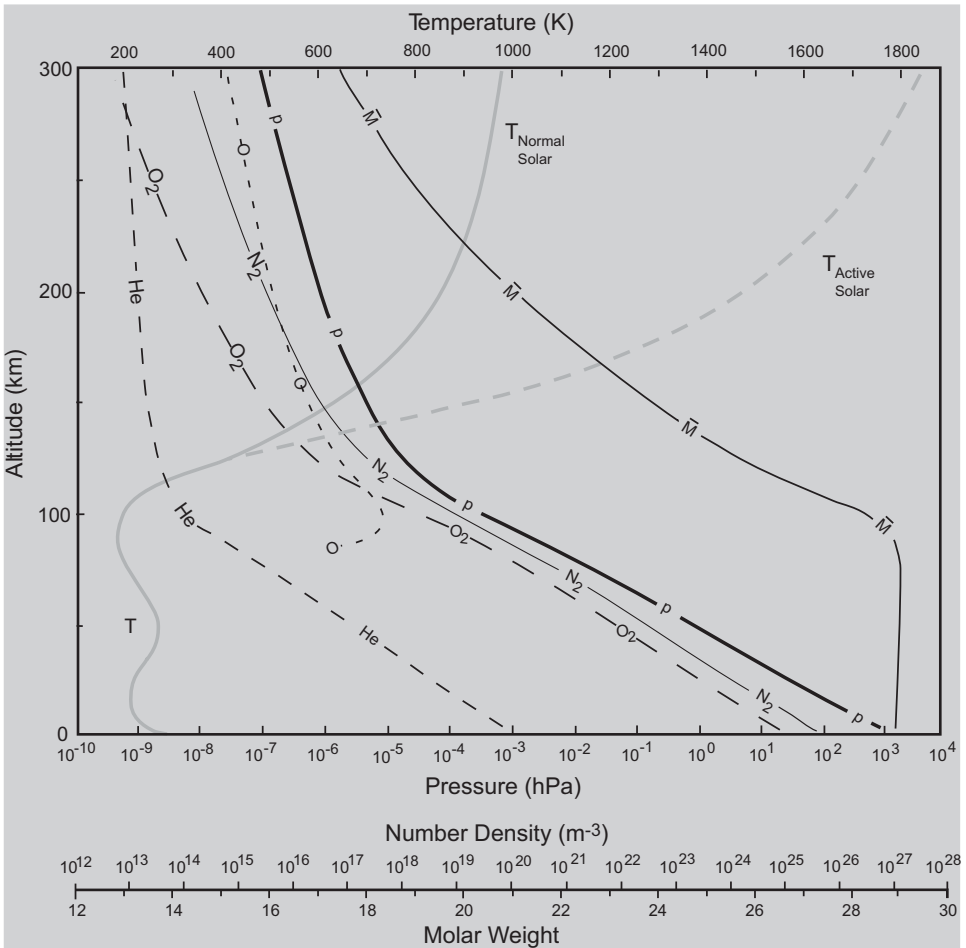


Figure 1.3 Global-mean pressure (bold), temperature (stippled), mean molar weight (solid), and number densities of atmospheric constituents as functions of altitude. *Source: U.S. Standard Atmosphere (1976).*

passive constituents are therefore homogeneous in this region. Those constituents are said to be “well mixed.” The densities of passive constituents then all decrease with altitude at the same exponential rate. This gives air a homogeneous composition, with constant mixing ratios $r_{N_2} \cong 0.78$, $r_{O_2} \cong 0.21$, and the constant gas properties³

$$M_d = 28.96 \text{ g mol}^{-1} \tag{1.18.1}$$

$$R_d = 287.05 \text{ J kg}^{-1} \text{ K}^{-1}. \tag{1.18.2}$$

The well-mixed region below 100 km is known as the *homosphere*.

³ Properties of dry air are tabulated in Appendix B, along with other thermodynamic constants.